



DESCRIPTION

COS TREATMENT APPARATUS AND
COS TREATMENT METHOD FOR GASIFIED GAS

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Technical Field

The present invention relates to an apparatus for removing COS (carbonyl sulfide) from a gasified gas obtained from coal, heavy oil, and the like.

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Background Art

There has been a demand in recent years for effective utilization of low-grade fuel, such as coal and heavy oil, in view of the diversification that is seeing not only high-
15 grade fossil fuel but also low-grade fossil fuel being actively used. Also, in the field of thermal power generation, from a view point of increasing power generation efficiency, combined cycle power generation in which a gas turbine using a gas fuel and a steam turbine are both used
20 and power generation in which hydrocarbon gas is introduced to a fuel cell have come into wide use. In such a situation, research and development have been carried out to utilize a gasified low-grade fuel for power generation.

Since low-grade fuel generally contains a large amount
25 of sulfur compounds, if it is gasified and burned without

being subjected to treatment, the sulfur compounds are exhausted as sulfur oxides into the air through a stack, which causes environmental degradation such as acid rain. Therefore, in ordinary thermal power generation, what is
5 done in practice is to provide an exhaust gas desulfurizer on the downstream side of a boiler for removing the sulfur compounds, for example, as gypsum. However, in the combined cycle power generation, materials are markedly corroded because the temperature at the inlet of the gas turbine is
10 higher than the temperature of the boiler in the ordinary thermal power generation. To solve this problem, it is necessary to protect the materials by removing various kinds of impurities including sulfur compounds on the upstream side, not on the downstream side, of the gas turbine, which
15 means that the aforementioned exhaust gas desulfurizer cannot be used. In fuel cell power generation as well, the securing of power generation efficiency and durability for the protection of materials is a must, and it is necessary to remove various kinds of impurities on the upstream side
20 of the fuel cell.

As a method for removing the impurities, what is called a wet-type gas purifying process, in which water-soluble components are removed with a water scrubber and H_2S (hydrogen sulfide) is removed with an aqueous solution of
25 amines, has been used in actual practice. However, the

aqueous solution of amines is incapable of removing COS,
although it is capable of removing H₂S. Therefore,
hydrolysis expressed by Formula (1) is carried out using a
COS conversion catalyst to accelerate a reaction in which
5 COS is converted to a form of H₂S that can be removed with
the aqueous solution of amines.



As a COS conversion catalyst, a catalyst containing
titania (refer to Japanese Patent No. 1463827, Japanese
10 Patent Provisional Publication No. 11-80760 (No. 80760/1999),
etc.), a catalyst containing alumina, a group IV metal, and
barium, and a catalyst containing an alkali metal, chromium
oxide, and alumina are known (Japanese Patent Provisional
Publication No. 2000-248286). However, these catalysts have
15 a problem in that catalytic activity is decreased by
unburned O₂ that is present in minute quantities (in the
order of ppm) in the gasified gas. Also, since nitrogen
that is introduced from the outside to provide a seal also
contains a minute quantity of O₂, the problem of decreased
20 catalytic activity becomes more serious.

In order to prevent the decrease in activity of the
COS conversion catalyst due to the O₂, a process in which a
combustion catalyst is provided on the upstream side of the
COS conversion catalyst has also been devised. However,
25 this process has some problems in that the combustion

catalyst is expensive because it generally carries a noble metal, the combustion catalyst is prone to be poisoned by H₂S and thus cause a decrease in performance, and heat generation on the combustion catalyst gives great stress to
5 the peripheral equipment.

Summary of the Invention

An object of the present invention is to protect peripheral equipment by relieving heat generation stress and
10 to protect a COS conversion catalyst from O₂.

The present invention is characterized in that by installing an O₂ removal catalyst for accelerating the reaction in Formula (2) on the upstream side of the COS conversion catalyst, O₂ is removed, and a decrease in
15 performance of COS conversion catalyst is prevented.



The inventors compared the merits of maintaining catalytic activity by removing O₂ with the demerits of increasing the load of catalyst by synthesizing COS. As a
20 result, the inventors discovered that the former is greater, and thus found the significance of accelerating the reaction in Formula (2).

The present invention provides a COS treatment apparatus for a gasified gas containing H₂S, H₂O, O₂, and CO,
25 characterized in that an O₂ removal catalyst and a COS

conversion catalyst located on the downstream side of a gasified gas flow with respect to the O₂ removal catalyst are provided.

According to the COS treatment apparatus provided with the O₂ removal catalyst in accordance with the present invention, since a decrease in activity of COS conversion catalyst due to O₂ can be prevented, an adverse influence exerted by unburned O₂ that is not fixed depending on the operation state of a gasification furnace and O₂ in the air, which is intentionally introduced to provide a seal, can be avoided. Also, a combustion catalyst that is expensive and short in service life and causes thermal stress is not used to remove O₂, so that a reduction in cost and an increase in reliability can be achieved.

Also, the present invention provides a COS treatment method for a gasified gas containing H₂S, H₂O, O₂, and CO, characterized by including a first step in which O₂ is removed by the reaction with H₂S and CO, and a second step in which COS is converted to H₂S.

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Brief Description of the Drawings

Figure 1 is a diagram showing one example of a flow of a wet-type gas purifying system to which the present invention is suitably applied;

25 Figure 2 is a view showing an example of arrangement

of an O₂ removal catalyst and a COS conversion catalyst in examples 1 and 2 of the present invention, wherein both of the catalysts are arranged in individual reactors;

Figure 3 is a view showing an example of arrangement
5 of an O₂ removal catalyst and a COS conversion catalyst in examples 1 and 2 of the present invention, wherein both of the catalysts are arranged in a single reactor;

Figure 4 is a view showing an example in which a COS conversion catalyst, which is also used as an O₂ removal
10 catalyst, in example 3 of the present invention is arranged in a reactor; and

Figure 5 is a graph showing a result of comparison of O₂ removal performance at the time when a gas temperature is changed in example 4 of the present invention.

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Detailed Description of the Invention

An embodiment of a COS treatment apparatus in accordance with the present invention will be described with reference to Figures 1 to 4.

20 Figure 1 is a diagram showing one example of a flow including a gasification furnace 3 and a wet-type gas purifying system to which the present invention is suitably applied. The gasification furnace 3 is a publicly known one, in which low-grade fuel 1, such as coal and heavy oil, and
25 oxygen, air, or oxygen enriched air, which is a gasifying

agent 2, are charged, and gasified gas 4 is taken out. From the taken-out gasified gas, dust is preferably removed by using a publicly known dust collector 5. A first heat exchanger 6 provided between the dust collector 5 and a COS treatment apparatus 7 gives heat that the gasified gas before purification has to the gasified gas after purification. The type of heat exchanger is not subject to any special restriction, and a generally used multitubular heat exchanger is used. The COS treatment apparatus 7 converts COS, which cannot be absorbed by a H_2S absorption tower 11, described later, to H_2S . In the conventional technique, the COS treatment apparatus 7 has been charged with only a COS conversion catalyst in a reactor. On the other hand, in the present invention, the COS treatment apparatus 7 is characterized by being charged with a combination of an O_2 removal catalyst and a COS conversion catalyst or a COS conversion catalyst that also has a function of O_2 removal. In Figure 1, the O_2 removal catalyst is placed at an upper part of the COS treatment apparatus, and the COS conversion catalyst is placed at a lower part thereof, by which the gasified gas is introduced from the upper part, and the treated gas is taken out from the lower part.

The O_2 removal catalyst is preferably installed under a high-temperature condition as described later in examples.

On the other hand, the COS conversion catalyst must be installed in the optimum service temperature region depending on the properties of gas to be treated in the service temperature range of 200 to 400°C, because at
5 equilibrium of the COS conversion reaction shown in Formula (1), the reaction toward the left-hand side is predominant when the temperature is high. Therefore, a mode is possible in which the O₂ removal catalyst is installed, for example, just behind the dust collector 5 of a higher temperature
10 without interposing a heat exchanger therebetween so as to be separated from the COS conversion catalyst. Since the performance of O₂ removal catalyst increases at high temperatures, the necessary catalyst charging amount can be decreased by installing the O₂ removal catalyst in a high-
15 temperature atmosphere. At this time, the first heat exchanger 6 can be installed behind the O₂ removal catalyst. However, the number of pressure vessels for charging catalyst is increased by installing the O₂ removal catalyst separately from the COS catalyst, so that cost is studied
20 according to the properties of gas to be treated, by which the optimum arrangement must be determined.

The arrangement of catalysts of one kind or two kinds in the present invention will be described later with reference to Figures 2 to 4.

25 Since the method for charging the catalyst is not

subject to any special restriction, a publicly known method, for example, a method in which a granular or honeycomb-shaped catalyst is housed in a proper reactor can be used. Also, the O_2 removal catalyst is not subject to any special
5 restriction as long as it acts to accelerate the chemical reaction in Formula (2). For example, a catalyst containing chromium oxide or nickel oxide, barium, and titania can be used, and in particular, a honeycomb-shaped TiO_2 catalyst carrying Cr_2O_3 and barium is preferably used.

10 The COS conversion catalyst is not subject to any special restriction as long as it acts to accelerate the chemical reaction in Formula (1). For example, a catalyst containing alumina, a group IV metal, and barium with Al_2O_3 or TiO_2 being a carrier, a catalyst containing an alkali
15 metal, chromium oxide, and alumina, or a catalyst containing barium and TiO_2 can be used. Among these, a honeycomb-shaped TiO_2 catalyst carrying barium is preferably used. The preferred amount of addition of Cr_2O_3 at the time when TiO_2 is used as a carrier is not smaller than 0.1 wt% and
20 not larger than 6 wt%, and is further preferably not smaller than 3 wt% and not larger than 6 wt%. The preferred amount of addition of NiO at the time when TiO_2 is used as a carrier is not smaller than 0.1 wt% and not larger than 15 wt%, and is further preferably not smaller than 5 wt% and
25 not larger than 10 wt%. The preferred amount of addition of

BaO at the time when TiO_2 is used as a carrier is not smaller than 0.1 wt% and not larger than 10 wt%, and is further preferably not smaller than 3 wt% and not larger than 6 wt%.

5 A second heat exchanger 8 provided between the COS treatment apparatus 7 and a gas cooling tower 9 serves, like the first heat exchanger 6, to give heat that the gasified gas before purification has to the gasified gas after purification. The gasified gas after purification passes
10 through the second heat exchanger 8 first and the first heat exchanger 6 next, by which a counterflow is formed with respect to the gasified gas before purification. Since a large average temperature difference can be secured as compared with the case of parallel flow, the heat exchangers
15 can be designed so as to be small in size, which is advantageous in terms of economy.

 The gasified gas before purification, which has passed through the second heat exchanger 8, goes into a water scrubber 10, where water-soluble impurities are removed from
20 the gasified gas. Preferably, another water scrubber 9 is provided between the second heat exchanger 8 and the water scrubber 10 to raise the solubility of water-soluble impurities with respect to the circulating water of the water scrubber 10. As the water scrubber 9, a water
25 scrubber having the same construction as that of the water

scrubber 10 can be used. The circulating water in which impurities are dissolved is discharged to the outside of the system through a discharge line, not shown, and make-up water corresponding to the discharge amount is supplied
5 through a make-up water line, not shown. As the water scrubber 9, 10, a publicly known water scrubber can be used.

The gasified gas having come out of the water scrubber 10 goes into the H_2S absorption tower 11, where the gasified gas comes into gas-liquid contact with a fresh absorbing
10 solution consisting of aqueous solution of amine compound. H_2S in the gasified gas is absorbed in the aqueous solution of amine compound. The gasified gas is taken out as a purified gas suitable as a fuel for a power generation apparatus such as a gas turbine and fuel cell. The purified
15 gas is heated by obtaining heat from the gasified gas before purification in the aforementioned second heat exchanger 8 and first heat exchanger 6, and therefore is utilized as a fuel having higher power generation efficiency. The absorbing solution having absorbed H_2S is sent to an
20 absorbing solution regeneration tower 12, where the absorbing solution is separated into fresh absorbing solution and high-concentration H_2S 15 by heat given by a absorbing solution regeneration heat source 14. The fresh amine compound returns to the H_2S absorption tower 11 to be
25 reused. The high-concentration H_2S 15 can be used as a raw

material for elemental sulfur, gypsum, sulfuric acid, and the like, and does not act as an environmental degradation source. As the H₂S absorption tower 11, absorbing solution regeneration tower 12, and absorbing solution, publicly
5 known ones can be used. Also, as the apparatus and method for manufacturing a valuable substance such as elemental sulfur, gypsum, sulfuric acid, and the like, publicly known ones can be used.

Figures 2 to 4 are views in which attention is paid to
10 the COS treatment apparatus 7 in accordance with the present invention. Figure 2 shows an example in which a first reactor 21 provided with an O₂ removal catalyst 22 therein and a second reactor 21' provided with a COS conversion catalyst 23 therein, which is disposed on the downstream
15 side of the first reactor 21, are combined. Figure 3 shows an example in which a single reactor 21 is provided therein with the O₂ removal catalyst 22 on the upstream side of the gasified gas flow and the COS conversion catalyst 23 on the downstream side thereof. Figure 4 shows an example in which
20 a reactor 21 is provided therein with a combinedly used COS conversion catalyst 24 that also has a function of O₂ removal. As the combinedly used COS conversion catalyst, a catalyst containing Cr₂O₃, barium, and TiO₂ can be used. In particular, a TiO₂ catalyst carrying Cr₂O₃ and BaO is
25 preferable because it is a catalyst which accelerates both

reactions of O₂ removal and COS conversion. Figure 5 shows a result of comparison of O₂ removal performance at the time when the gas temperature is changed.

Examples

5 COS conversion rates at the time when COS of 307 ppm was charged were compared by unifying the sum of O₂ removal catalyst and COS conversion catalyst into $SV = 4528 \text{ [1/h]}$. As the result, the data shown in examples 1 to 3 in Table 1 were obtained. SV is a space velocity, and its unit is the
10 inverse number of time. Also, the conditions under which the O₂ removal performance of O₂ removal catalyst was compared by changing the gas temperature are shown in example 4 in Table 1.

[Example 1]

15 TiO₂ carrying Cr₂O₃ (in Table 1, described as Cr/TiO₂) was used as the O₂ removal catalyst, and TiO₂ carrying BaO (in Table 1, described as Ba/TiO₂) was used as the COS conversion catalyst on the downstream side of the O₂ removal catalyst. As a result, the COS concentration on the COS
20 conversion catalyst outlet side was 12 ppm, and the COS conversion rate was 0.961.

[Example 2]

 TiO₂ carrying NiO (in Table 1, described as Ni/TiO₂) was used as the O₂ removal catalyst, and TiO₂ carrying BaO
25 was used as the COS conversion catalyst on the downstream

side of the O₂ removal catalyst. As the result, the COS concentration on the COS conversion catalyst outlet side was 14 ppm, and the COS conversion rate was 0.954.

[Example 3]

5 TiO₂ carrying Cr₂O₃ was used as the combinedly used COS conversion catalyst that has both functions of O₂ removal catalyst and COS conversion catalyst. As the result, the COS concentration on the COS conversion catalyst outlet side was 15 ppm, and the COS conversion rate was 0.951.

10 [Comparative example]

 The O₂ removal catalyst was not used, and TiO₂ carrying BaO was used as the COS conversion catalyst. As the result, the COS concentration on the COS conversion catalyst outlet side was 110 ppm, and the COS conversion
15 rate was 0.642.

[Example 4]

 An experiment was performed to compare the O₂ removal performance of the O₂ removal catalyst by changing the gas temperature. As the result, it was found that the
20 performance increases with increasing temperature as shown in Figure 5.

Table 1 Results of experiment

	Item	Unit	Example 1	Example 2	Example 3	Comparative example	Example 4	
Inlet gas condition	H ₂	Vol-%	12.6					
	H ₂ O	Vol-%	3.1					
	CO	Vol-%	28.4					
	CO ₂	Vol-%	4.2					
	N ₂	—	Balance					
	H ₂ S	Ppm-v	567					
	COS	Ppm-v	307					
	O ₂	Ppm-v	145				240	
	Temperature	°C	300				200~400	
	Pressure	Mpa	2.29					
Catalyst condition	O ₂ removal catalyst	Kind	—	5.5wt%C r2O3/TiO ₂	10wt%NiO/TiO ₂	5.5wt%C r2O3/TiO ₂	None	5.5wt%C r2O3/TiO ₂
		SV	1/h	11320		4528	—	30000
	COS conversion catalyst	Kind	—	4wt%BaO/TiO ₂		(O ₂ removal catalyst was combinedly used)	4wt%BaO/TiO ₂	None
		SV	1/h	7547			4528	—
	Sum of catalysts	SV	1/h	4528				30000
	Outlet gas component	H ₂ S	ppm-v	862	860	859	764	—
COS		ppm-v	12	14	15	110	—	
Performance	COS conversion rate*	—	0.961	0.954	0.951	0.642	—	

Vol% is percentage by volume, and ppm-v is parts per million by volume.

*COS conversion rate = (inlet COS concentration - outlet COS concentration)/inlet COS concentration

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Industrial Applicability

The COS treatment apparatus and COS treatment method for a gasified gas in accordance with the present invention can suitably be applied to power generation having high power generation efficiency in the field of thermal power generation such as combined cycle power generation in which a low-grade fossil fuel such as coal and heavy oil is gasified, and a gas turbine using a gas fuel and a steam turbine are both used, or power generation in which hydrocarbon gas is introduced to a fuel cell.

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